

ION EXCHANGE CASE STUDY

by

Robert S. Welther  
Creative Engineering Laboratory  
Massachusetts Institute of Technology

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# ION EXCHANGE AND ITS APPLICATION TO THE CONTINUOUS COUNTERCURRENT PROCESS

## I. Introduction

### A. Background

Because of the rapid depletion of reserves of ferrous and non-ferrous metals, there is a real need for technological improvements in the recovery of metals from low grade ores. Furthermore, metals now needlessly going to waste should be recovered. Ion exchange techniques appear to be destined to play a role in realizing these objectives, since ion exchange resins have the ability to concentrate traces of metals from dilute solutions and also recover metals that are difficult to separate.

In mineral engineering the first industrial use of ion exchange resins has been to recover uranium from South African gold ores. (1, 2, 3). Ion exchange also offers real promise in the recovery of other metals from ore pulps if a practical method can be found by which the ion exchange resin can be placed in the ore pulp for adsorption of metal ions followed by separation of the resin from the pulp for subsequent metal recovery. This may make the processing of low grade ores economical, because of the resulting savings in investment, labor, pumping, filtration and tailing loss.

It is the desired development of this resin-in-pulp operation which serves as the nucleation of this report.

### B. Purpose of Report

In dealing with the subject of ion exchange, the following report has a two-fold purpose. Primarily it is intended as a case study report to be used as the foundation for a design project in the Creative Engineering course sponsored by the Mechanical Engineering Department. This design project will be aimed at the development of a means for effecting continuous countercurrent ion exchange for the treatment of low grade ore pulps. The second, and equally important purpose of this report, is to serve as a source of reference material

to aid the Mineral Engineering Department in their current development of ion exchange methods for the recovery of metals from low grade ore pulps.

In view of the two objectives listed above, the scope of this report has been primarily limited to the presentation of information dealing with continuous countercurrent ion exchange. This information, however, has been prefaced by a discussion of ion exchange in general, in order to include information which quite possibly will be useful to the mechanical engineer in solving the aforementioned problem, i.e. the development of a practical apparatus for continuously moving an ion exchange resin countercurrently to the flow of an ore pulp, in order to recover the metal values from the ore.

## II. Ion Exchange in General

The purpose of this section is to provide the mechanical engineer with background information which may be helpful in developing a practical continuous countercurrent ion exchange system. (4, 5, 6, 7, 8, 9, )

### A. Brief History of Ion Exchange

Ion exchange may be defined as an operation in which either the anions or the cations of a substance are reversibly replaced by ions of similar charge. Credit for the recognition of the phenomenon of ion exchange is generally attributed to H. S. Thompson and J. Thomas Way, two English agricultural chemists. In 1848, Thompson reported to Way that, on treating a soil with either ammonium sulfate or ammonium carbonate, most of the ammonia was adsorbed and lime was released. The extensive experiments which Way then conducted in the years 1850 to 1854 represent the first systematic study of ion exchange, and no further contributions were made towards an understanding of this reaction for several decades.

Around the beginning of the nineteenth century, R. Gans proposed, as a result of his classic studies, the use of ion exchange for industrial purposes. Gans believed that both natural and synthetic aluminum silicates could be employed economically for softening waters and for treating sugar solutions.

As time went on, however, the limitations of siliceous ion exchangers became more and more evident as commercial exploitation of these substances was attempted. In 1935, B. A. Adams and E. L. Holmes (12) observed that certain synthetic resins were capable of exchanging ions. The versatility of these resins was rapidly recognized by many academic and industrial chemists, with the result that a large number of new and unique uses were found for ion exchange.

Since then, the world has experienced the rapid growth in the use of ion exchange to its present importance as a valuable unit operation for modern industry and a powerful tool for the research chemist.

### B. Ion Exchange Theory (9)

A cation exchange may be looked upon as a giant anion with a framework structure containing exchangeable cations. Because of this porous structure, (of ionic dimensions) cations can migrate in and out of the particle and can be exchanged for different cations. Similarly, an anion exchanger particle is merely a giant cation.

Such a structure as above is found in nature in the zeolite minerals. Indeed, at one time, the zeolites were so closely identified with ion exchange that the term "zeolite" was extended to include all ion exchanging substances. This usage persists even today, except for the organic exchangers discovered by Adams and Holmes, and the ion exchange process for softening water is usually called the "zeolite process", even though true zeolites are never used for this process, because their ion exchanging capacity is too low for practical use.

An example of a true zeolite is natrolite,  $\text{Na}_2 \text{Al}_2 \text{Si}_3 \text{O}_{10}$ . The negative ions of natrolite are not single  $\text{Al}_2 \text{Si}_3 \text{O}_{10}$  groups, but are an endless three dimensional framework, in which this unit of two Al, three Si, and ten O atoms occurs repeatedly, like the pattern on wallpaper. Two out of every ten oxygen atoms bear a negative charge. This particular framework has three sets of parallel channels at right angles to each other, running through the whole crystal. The sodium ions reside in these channels, their positive charges exactly neutralizing the fixed negative charges of the aluminosilicate

framework (13). Because of the channelled structure, the sodium ions can easily move out, but when they do move out, other positively charged ions must move in to take their place, or the negative charges of the framework will not be neutralized. A potassium ion can move in and displace a sodium ion, or a calcium ion with its double charge can displace two sodium ions, and so on. This is the process of ion exchange.

The nature of ion exchange can be further illustrated by considering the softening of water by means of ion exchange. In this operation, hard water, containing harmful calcium or magnesium ions, is allowed to flow down through a bed of cation-exchange particles containing exchangeable sodium ions. Calcium and magnesium ions enter the particles and release sodium ions.

The principle of this column type of operation is illustrated in Figure 1. After a certain amount of solution has been introduced into the column, the upper part of the exchanger bed is saturated with the calcium ions whereas the lower portion is still in the sodium form. Therefore, in the upper portion of the bed the concentration of calcium ions in the solution is the same as in the influent  $C_0$ , whereas in the lower portion the concentration of calcium is zero. In the boundary zone the concentration of  $Ca^{++}$  in solution changes gradually from  $C_0$  to zero. The effluent solution contains sodium ions only, which are not harmful since they form neither a scum with soap nor scale in steam boilers. When calcium ions are detected in the effluent of the column, the so-called "break-through" point has been reached, which means all the resin in the column is saturated with  $Ca^{++}$ . The operation is then reversed and the bed is "re-generated" by passing a concentrated sodium chloride solution through the column. About ten minutes contact is usually sufficient for all the calcium and magnesium ions to be removed from the bed, being replaced by the excess of sodium ions in the salt brine solution (9). Following regeneration, the residual salt solution is removed from the bed by a fresh water rinse and the bed is then ready to soften more water. In industrial water softening installations, ion exchangers have been through thousands of cycles of this kind without any deterioration (9).

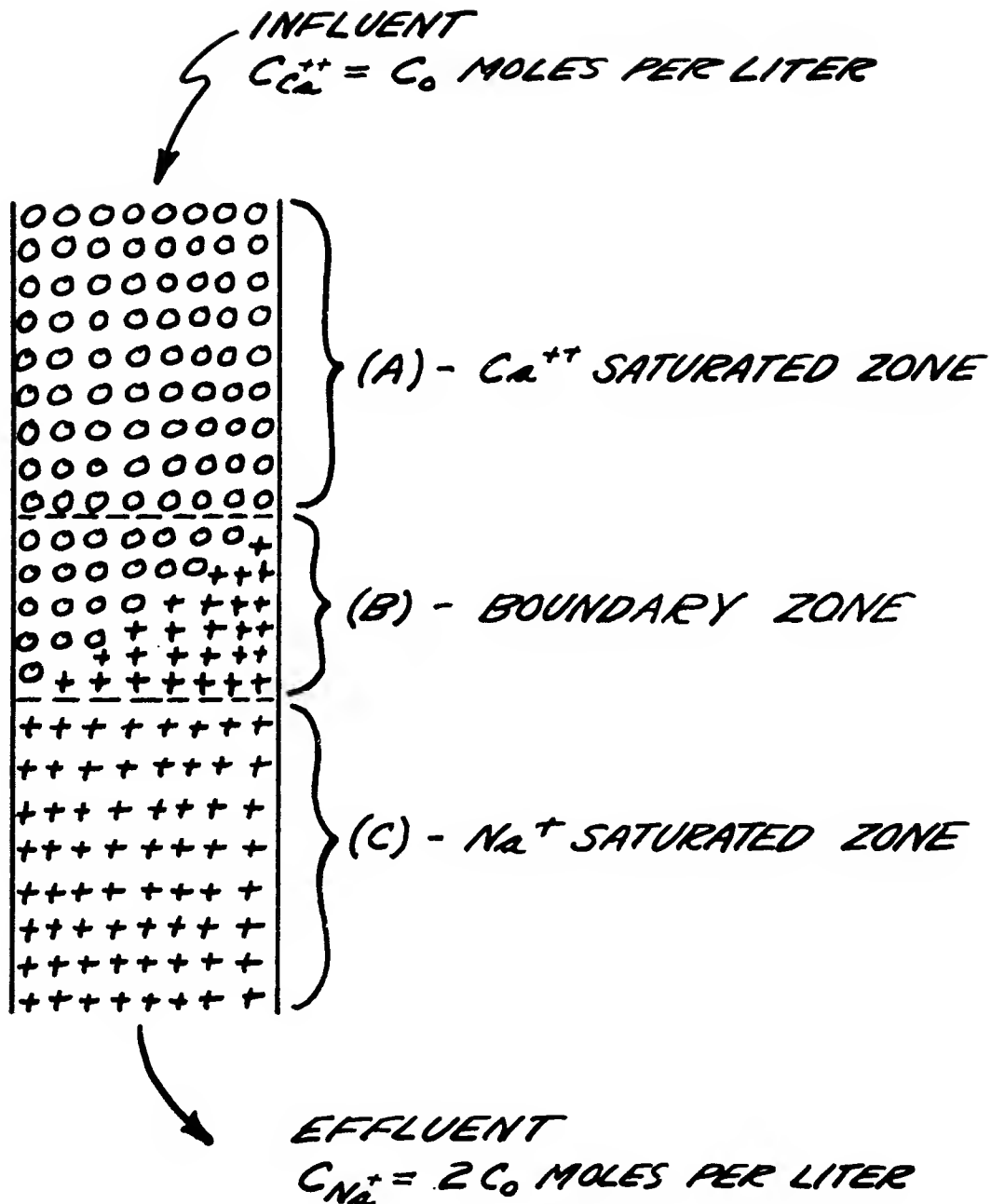
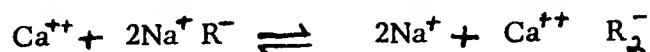


FIGURE 1 - SCHEMATIC DIAGRAM ILLUSTRATING THE PRINCIPLE OF COLUMN OPERATION

C. Ion Exchange Kinetics and Equilibrium (13, 14, 15, 16, 17)

Ion exchange is a typical reversible reaction. The exchange of calcium for sodium ions as in the water softening process above can be represented by the equation:



where R represents the exchange resin and the equilibrium obeys the mass-action law:

$$\frac{[\text{Na}^+]^2 \text{ in solution } [\text{Ca}^{++}] \text{ in exchanger}}{[\text{Ca}^{++}] \text{ in solution } [\text{Na}^+]^2 \text{ in exchanger}} = K$$

where K is a constant known as the "equilibrium constant". The quantities in brackets are the activities of the substances rather than the concentrations, although the molar concentrations in the exchanger can be introduced without much error. The equilibrium constant depends on the exchanger, being about three for a particular carbonaceous cation exchanger known commercially as "Zeo-Karb" which is used quite extensively for water softening. (18) The equilibrium constant of three means that this exchanger prefers calcium ions to sodium ions, other things being equal, but not by very much. In general, the higher the valence of an ion and the less hydrated it is in solution, the more the ion is attracted to the exchanger. (19, 20) Correlations between equilibrium constant and ionic radius have also been noted, up to a point, the larger the unsolvated ion, the better it is held by an exchanger. (19)

Temperature has very little influence on the equilibrium, showing that there is very little heat of reaction in ion exchange. (21) Ion exchange can be a very fast process requiring only about thirty minutes for 90 percent completion in the treatment of a copper sulfate solution with a commercial cation exchanger, or the process may be much slower, which is usually the case with anion exchange, which may require as much as from three to twenty-four hours for 90 percent completion in the removal of HCl from solution depending upon the exchanger used. (15) The speed of ion exchange depends greatly on the porosity

of the exchanger, since porosity controls the diffusion rate of ions inside the resin particle.

#### D. Ion Exchangers (4, 22, 23)

From the standpoint of physical structure, ion exchangers are extremely insoluble porous materials whose walls contain a high percentage of tightly bound exchange groups. In appearance they are usually granular solids, in sizes ranging from 10 to 70 mesh and may vary in color from white to black. Densities of organic exchangers when shipped may range from 30 to 50 pounds per cubic foot.

Although exchange capacity is usually stressed, a number of other factors are just as important in evaluating these materials. Some of these include:

1. Degree of removal of ions from solution.
2. Chemical requirements for regeneration.
3. Flow rates or throughput in packed beds.
4. Chemical and physical stability.

The majority of the ion exchangers used today may be classified into the following general categories: (24)

1. Cation exchangers
  - a. Zeolites ( natural or synthetic siliceous compounds)
  - b. Carbonaceous Zeolites (sulfonated coals, etc.)
  - c. Resinous (generally phenol-formaldehyde types)
2. Anion exchangers
  - a. Inorganic (dolomite, heavy metal silicates)
  - b. Organic (amine-formaldehyde resins, etc.)

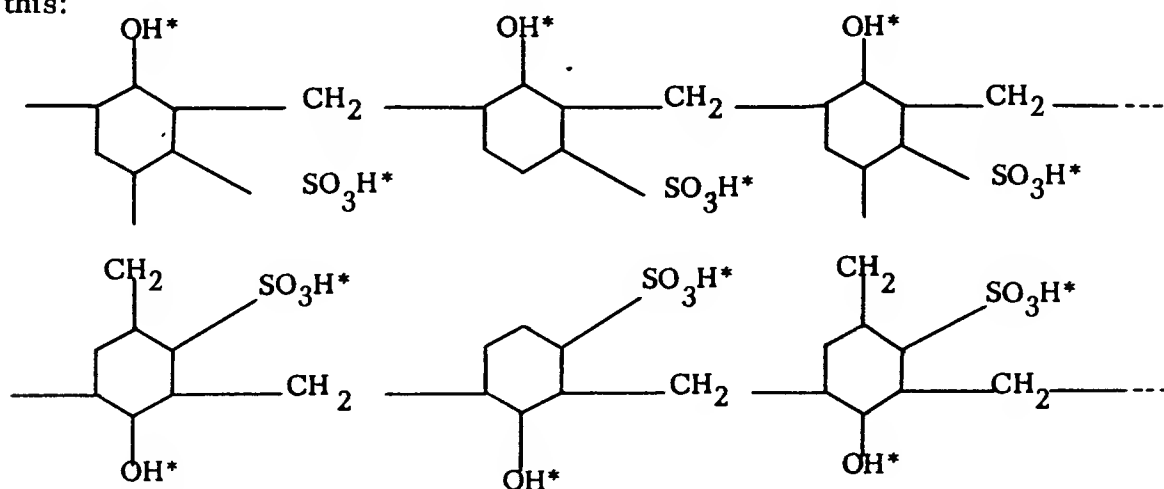
Insofar as special applications are concerned, such as metal recovery from solutions, the most important types of exchangers are the carbonaceous and resinous cation exchangers and the organic anion exchangers. The well-established unit operations however, such as water softening, sugar solution treatment and demineralization generally make use of the zeolites and anion exchangers.



1. Cation Exchangers (9)

The carbonaceous or sulfonated coal type cation exchangers are used primarily because of their cheapness and chemical stability. This type of ion exchangers can be made by treating bituminous coal with fuming sulfuric acid or sulfur trioxide. (25) Oxidation and sulfonation take place, and the product has sulfonic acid, carboxyl, and phenolic groups attached to a framework of fused benzene rings. These sulfonated coals generally do not have the capacity of the more recently developed sulfonic acid resins.

The last, but most versatile class of cation exchangers are those of the resinous type. This is the class of exchangers which was discovered by Adams and Holmes in 1935, and which has since opened up many new fields to ion exchange. One type of cation exchange resin can be prepared by mixing concentrated solutions of phenolsulfonic acid and formaldehyde in the presence of an acid catalyst. In the course of the chemical reaction which results, the ingredients set to a brown or black gel which dries to a porous mass containing replaceable hydrogen ions. This exchanger has a chemical structure something like this:



\* Exchangeable cations.

The benzene rings are tied together in an endless insoluble framework, but the hydrogen ions of the sulfonic acid groups ( $\text{SO}_3\text{H}$ ) and, to a smaller extent, those of the phenolic hydroxyls, are free to be replaced by any other

cations. The revolutionary importance of these cation exchanger resins is that the hydrogen ion can be exchanged just like any other cation. This is not possible in the aluminosilicates because acids will attack these porous materials very rapidly, liberating silica. Certain other advantages of these resin exchangers are that they are usually more rapid in their action, and some of them have much higher capacity than the aluminosilicates. Also, they do not import any trace of silicate to the contacting solution, a characteristic which is undesirable when treating water for steam boilers.

## 2. Anion Exchangers (9)

The anion exchangers are less widely used than the cation exchangers, primarily because the ion exchanging processes requiring them are not as numerous as cation exchange processes. This seems also to be a valid explanation for the fact that somewhat less is known about anion exchange than cation exchange. However, their use is important in certain processes, particularly metal recovery processes involving the heavy and precious metals, since the metals are brought into solution by complexing the metal with anions.

The anion exchange resins, generally speaking, are synthesized to obtain the same fundamental properties as the cation exchange resins, i.e. a physically and chemically stable cross-linked network to which are attached exchangeable ionic groups. Anion exchange resins are usually produced by condensing a polyamine with formaldehyde to produce a progressive chemical structure, similar to the cation-exchange resin, the difference being that an  $\text{NH}_3$  group replaces the  $\text{SO}_3\text{H}$  group on the cation exchanger. In this case, the hydroxyl (OH) ions of each linked benzene ring are free to be replaced by any anions in solution.

## 3. Ion exchange Fabrics (26, 27)

In addition to the more common granular types of ion exchangers discussed above, certain chemically modified cotton fabrics have been developed which exhibit ion exchange properties similar to those of the ion exchange resins... (28, 29, 30, 31). These ion exchange cottons are made by the introduction of substitute groups with basic or acidic properties into the cellulose molecule under such conditions that the fabric structure is retained. Some of these cation cottons

have been found to have a total ion exchange capacity comparable with commercial resins and because of their fibrous structure their rates of exchange are considerably faster than resins. (26) The capacities of the anion exchange fabrics however, do not compare quite so favorably with the resins.

### E. Some Applications of Ion Exchange

No attempt will be made here to list and describe all the applications of ion exchange since these are too numerous for adequate coverage in a report of this size. The following applications therefore, are intended to serve as illustrations of some of the more well established and developed uses of ion exchange existing today.

#### 1. Water Softening (7, 9)

This is presently the largest single application of the ion exchange process. Many cities are now including the zeolite process on a large scale in their water treating plants in order to deliver to the public a higher purity water, or, in some cases, where the natural water supply is unusually hard, to provide water of tolerable hardness. Home water softening units are also becoming more popular, especially in the rural and mountain localities where natural waters contain large amounts of dissolved minerals. A significant recent advance in water treating which has been made possible by ion exchange is the complete removal of electrolytes from water without distillation. This process, known as demineralization, consists of first passing the water through a cation exchanger containing hydrogen ions. This converts the mineral salts in the water to weak acids of these salts. The water is then passed through an anion exchanger which removes the acids, leaving the water free from electrolyte. By employing this process, many industries today are using demineralized water which could not afford to use distilled water.

#### 2. Sugar Refining (4)

Because of the fact that the ion exchange process will not remove dissolved

impurities which are nonionized, such as sugar, it has found wide application in removing dissolved salts from sugar juices. By passing the sugar juices through ion exchange beds at various stages in the refining operation, it is possible to remove a greater portion of the dissolved ions than with regular methods. This makes possible the production of 96 to 98 percent pure sugar juices from which 95 percent of the total sugars can be recovered as white sugar. This is approximately ten percent better than with ordinary methods. In addition, the remaining molasses is an edible pleasant tasting syrup which is more readily marketable.

### 3. Metal Recovery (32, 33, 34, 35, 36, 37, 38, 39, 40)

Besides being capable of removing unwanted impurities, ion exchange is also capable of recovering valuable ionized substances from solution. For example, if a very dilute solution of a copper salt is passed through a cation exchanger bed, the copper ions are held back in the exchanger. By regenerating the exchanger with a two normal solution of sulfuric acid, the resulting effluent will be a relatively concentrated copper solution from which crystals of copper sulfate can easily be obtained. During World War II, German industry used an ion exchange operation to recover copper from cuprammonium wastes of rayon spinning plants. (7, 41) By using such an operation, the recovery of copper rose from 85 to 93 percent complete. Details of this operation are tabulated in Table I. In 1946, a similar method was about to be put into production by the Germans to recover silver from waste waters obtained by washing film coating equipment. (7) At the present time there is at least one plant in this country which uses cation exchange to recover zinc from viscose rayon plant acid waters. (39)

In the metallurgical field, applications of ion exchange resins include the recovery of tin, chromium, copper, zinc, and iron from pickling and plating solutions, (34, 37, 38), the prevention of pollution by waste effluents and the recovery of the constituents from them, (32, 35, 36, 42, 43, 44), and the purification of valuable metals such as the rare earths by chromatographic fractionation on columns of ion exchange resins (45, 46). Also, laboratory

experiments have shown that it is possible to separate copper, zinc, nickel, iron, gold, and silver from complex ores by means of anion exchange. (33)

TABLE I (7)

DATA CONCERNING CATION EXCHANGE COPPER RECOVERY UNITS AT  
DORMAGEN -- I. G. WERKE -- GERMANY

Equipment Data

Diameter	9.85 ft.
Cross-sectional area	75.3 sq. ft.
Resin bed depth	13.8 ft.
Resin volume	1025 cu. ft.
Resin weight	21 tons

Operational Data

Rate	1060 gal./min.
Rate	14.1 gal./min. /sq. ft.
Pressure drop	7.4 - 36.7 lb./sq. in.
Feed - Temperature	38° C
- Composition	(see below)
Regenerant - composition	(see below)
- dosage	0.28 lb. H <sub>2</sub> SO <sub>4</sub> /kilogram (as CaCO <sub>3</sub> ) of adsorbed copper.
Regeneration time	8 hours
Regenerant effluent	(see below)
Capacity of resin	tons of copper per unit per cycle - 45.1 kilograms ( as CaCO <sub>3</sub> ) per cu. ft. -- 3.14 meq./g/.

TYPICAL CONCENTRATION DATA (meq./l.)

	Copper	Ammonia	H <sub>2</sub> SO <sub>4</sub>
Feed-rayon waste water	2.8	41.2	
Feed-staple waste water	6.3	70.5	

	<u>Copper</u>	<u>Ammonia</u>	<u>H<sub>2</sub>SO<sub>4</sub></u>
Waste spinning acid (regenerant)	283	—	245
Regenerant effluent	378	—	61

For metal recovery applications the organic exchangers are much preferred to the inorganic, since the heavy metal ions tend to react with the aluminosilicate framework of inorganic exchangers and will not come out in regeneration.

#### 4. Recovery of Organic Compounds (7, 9)

The recovery of valuable substances by ion exchange has not been limited to metals alone. Ion exchangers have proven very successful in removing alkaloïds such as quinine and nicotine from solution. These substances form positive ions with the hydrogen ion and can be adsorbed very nicely on a hydrogen ion exchanger. They can then be removed from the exchanger by regeneration with alkali together with a suitable solvent, such as alcohol or acetone. (47) Vitamins can also be recovered in this way. The B complex, thiamin, which is strongly ionized, can be separated from riboflavin, which is weakly ionized and hence weakly adsorbed.

#### 5. Ion Exchange in Analytical Chemistry (7, 9)

A notorious difficulty in quantitative analysis is the exact determination of sulfate in solutions which also contain iron or aluminum. Barium sulfate precipitated from such solutions is always contaminated with iron or aluminum, while if the trivalent metals are precipitated first as hydrous oxides, these oxides carry down sulfate with them. The answer to the problem is to pass the solution through a hydrogen ion exchanger, so that the metal ions are retained by the exchanger and the sulfate is passed on as sulfuric acid in which the sulfate ion is easily and accurately determined. The metals can then be removed from the exchanger with hydrochloric acid and their amounts determined separately. Many other analytical separations are possible along these same lines. (16, 48, 49) In such work the sulfonated coal type exchangers are preferred to the resins because of their greater stability.

## 6. Miscellaneous Applications (4, 5, 7, 9, 23)

In addition to the more general applications mentioned above, there are many other more specific uses of the ion exchange process which have definite places of importance in the chemical processing industries, as well as the medical, biological and research fields. Some of these applications are:

1. Milk curd modification and recovery of lactose from milk whey. (5, 7)
2. Preparation and purification of colloidal solutions. (7)
3. Removal of copper and sodium from petroleum distillates and distillate residues. (4, 7)
4. Purification of ethylene glycol (antifreeze) and other polyalcohols. (4, 7)
5. Purification of formaldehyde solutions. (7)
6. Soilless growth of plants. (7)
7. Modification of the coagulative properties of blood for transfusion purposes. (7, 23)
8. Purification of biologically active substances - streptomycin, penicillin, etc. (4, 7)
9. Recovery of copper from cuprammonium textile wastes. (4, 7)
10. Desalting sea water. (7, 9)
11. Selective adsorption for separation of fission products and alkaline earths. (7, 16)
12. Organic and inorganic catalytic applications. (7)
13. Adsorbents in biochemical and physiological research. (7, 16)
14. Separation of amino acids. (7, 16)
15. Recovery of pectin from grapefruit peels. (4)
16. Titrate removal from grape wastes. (5)
17. Artificial aging of whiskey. (4)
18. Treatment of ulcers. (7)

From these examples it can be seen that ion exchange is no longer confined to the one major application of water softening, but rather is considered as a unit operation ranking in importance with filtration, distillation and the like.

## F. Ion Exchange Methods and Equipment

There are two general methods of ion exchange which are presently employed for most industrial and technical ion exchange processes. These are the batch and fixed bed methods.

### 1. Batch Exchange (50)

Of the two major ion exchange techniques, the simplest, as well as the first developed method, batch processing, has been the least used. This is partly due to the inconveniences involved in separating the resin and solution after exchange is completed, and partly because batch exchange does not remove enough ions in a single step.

Among the present batch processes of commercial interest, one has been used on a factory scale for a number of years in the production of pectin from grapefruit peel. (4) Another interesting batch application, studied on a pilot scale, is the heart of a process to recover gold from pregnant cyanide solutions of a leach pulp prepared from ore. (51)

a. Equipment. As one might expect, equipment used commercially for batch ion exchange has been adapted from ordinary stirred tanks and basket centrifuges already used in the process industries for contacting and separating liquids and solids. Along the same line, the stirred contactors and settling units normally used in hydrometallurgy for ore treatment were adapted for the gold recovery process above.

Recently, Stanford Research Institute developed a batch contactor on a small pilot plant scale, that combines both the agitation and filtration steps in the same tank and thus does not require movement of the resin from the tank, with possible resultant attrition. This so-called "mixer-settler" type batch unit consists of a tank with a perforated plate near the bottom to retain the resin, and a top and bottom outlet fitted with three-way plug valves, as shown in Figure 2. The steps of the operation in sequence are as follows:

1. Initially, the tank containing a given amount of exchange resin is empty of solution.



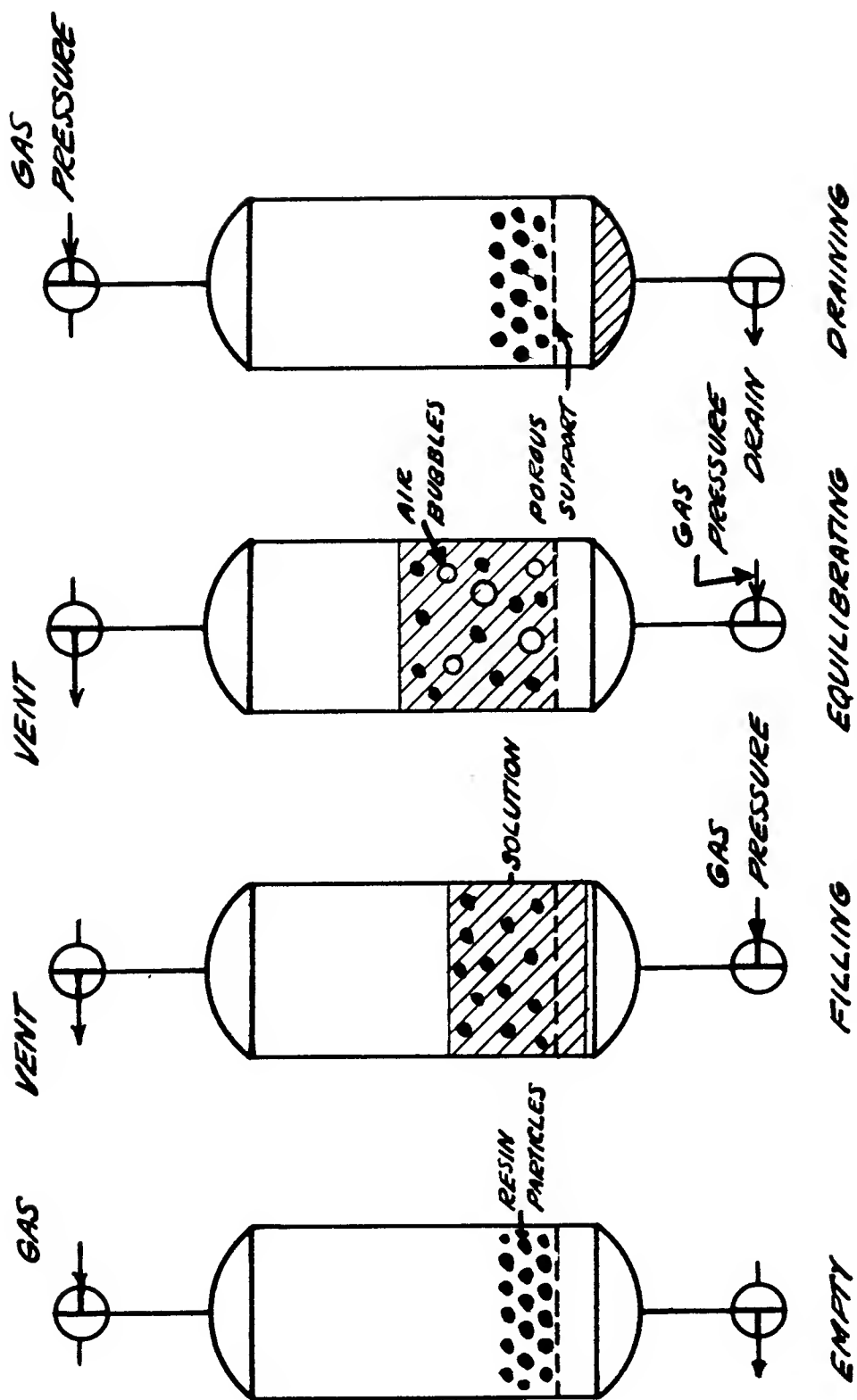


FIGURE 2 - SEQUENCE OF OPERATIONS IN A MIXER-SETTLER FOR ION-EXCHANGE

2. The cycle is started by forcing into the tank a measured amount of contacting solution. This is accomplished with the aid of gas pressure.
3. With the contacting solution in the tank, the gas pressure is continued, causing a flow of bubbles through the solution. The resulting agitation assists in bringing about equilibrium between the resin and solution.
4. Following equilibrium the gas flow is reversed, forcing the solution out of the tank and blowing the resin free of interstitial solution. The cycle can then be repeated.

This type of batch device can be regenerated, when necessary, in the same manner as the contacting process, only using regenerant instead of feed solution. Also, it may be used as a single unit, or a group of the mixer-settlers can be operated in a counter-current fashion by employing automatic cycling and sequencing controls. (52)

In designing units for batch exchange, the two most important factors to be considered are the time required for equilibrium and the solution-resin ratio. Usually the holding time for equilibrium can be limited to 20 to 30 minutes, if proper agitation of the mixture is maintained. The solution-resin ratio may vary from an absolute minimum of 3 gal./cu. ft. to as much as 110 gal./cu.ft. This ratio is limited on the low side by the thickness of the slurry to be agitated and on the high side by the efficiency of solution-resin contact. (50)

## 2. Fixed Bed Ion Exchange

Presently the ion exchange industry utilizes fixed bed operations almost exclusively, although there has started recently a gradual trend toward continuous counter-current exchange which is still more or less in the experimental stage. The term "fixed-bed" as applied to ion exchange implies the utilization of a packed column of stationary exchanger to process a solution in a cyclic manner. According to this interpretation, therefore, fixed bed exchange also includes mixed bed and ion exclusion processes. (53, 54)

a. Equipment. (50) To effect removal or recovery of ions, the normal fixed bed cycle consists of these steps:

1. Treatment (saturation) of the ion exchange bed with raw feed solution.

2. Backwashing of the bed to remove dirt, foreign matter, and to loosen and regrade the bed.
3. Regeneration of the exhausted exchanger by passing regenerant solution through the bed.
4. Rinsing the bed free of regenerant thus preparing it for next cycle.

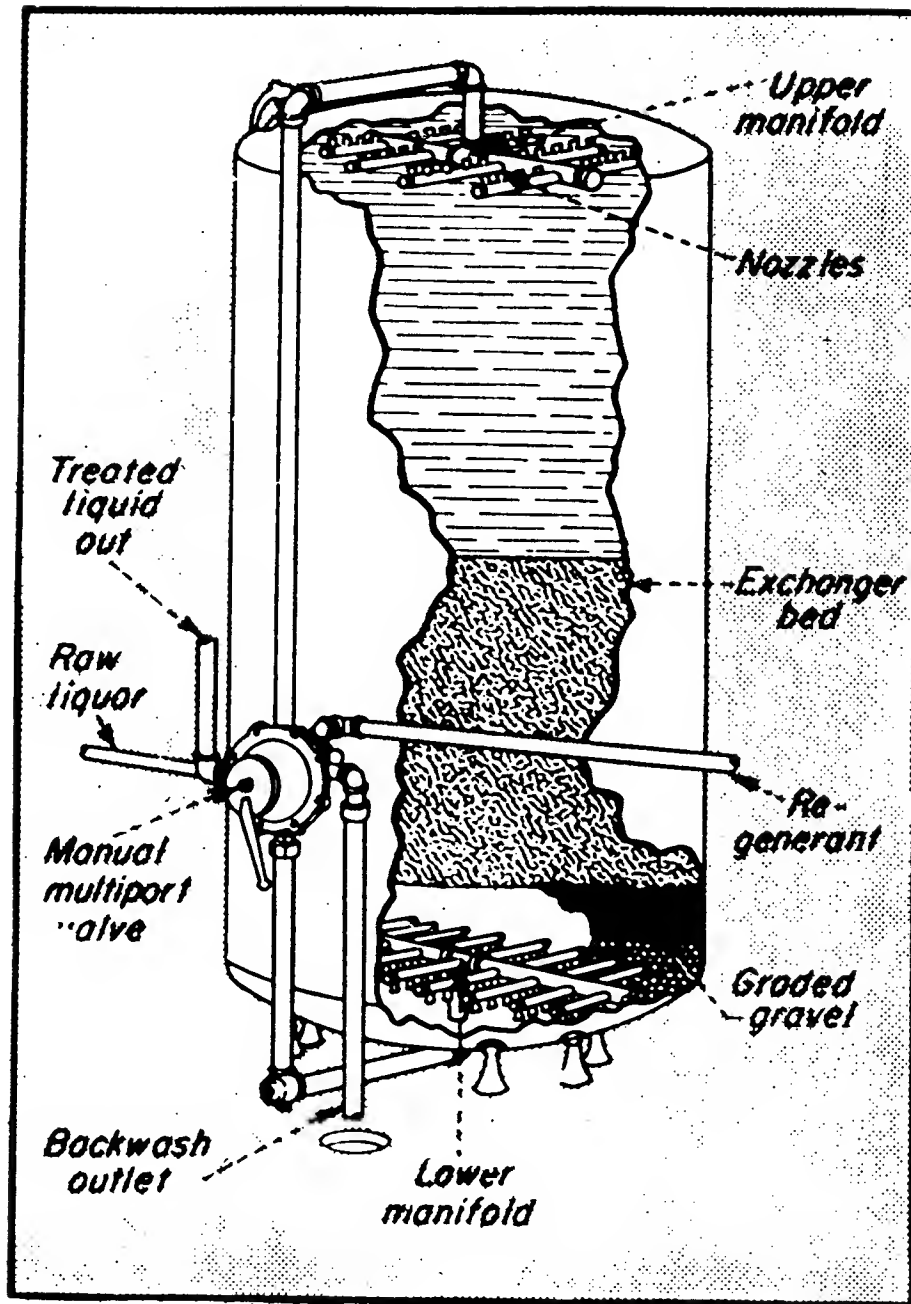
Both steps 2 and 4 above are usually comparatively short intervals of the entire cycle. In commercial installations of fixed bed units, usually two or more units are provided to insure a constant flow of treated solution, one unit treating while the other is being regenerated.

Fixed bed equipment is fairly standard in design, consisting of a cylindrical tank containing a bed of exchanger, supported on a false bottom or on built-up layers of graded gravel, quartz, or similar material as shown in Figure 3. A collector device is built under the false bottom while a system for distributing the feed solution and the regenerant is installed above the exchanger bed. An external piping system handles the flow of feed solution, regenerant solution, and backwash and rinse water.

One of the most critical elements of fixed bed equipment is the design of the distributing system because the feed solution must pass through the bed without channeling. Therefore uniform and efficient distribution of the feed, regenerant, backwash and rinse solutions is essential for economical and satisfactory operation. Perforated piping such as spiders, circular sparge pipes and laterals are used for both distribution and collection. The supporting bed prevents the fine granules of exchange material from passing out with the effluent. It also aids distribution of the backwash.

Either upflow or downflow of feed solution through the bed may be practiced, but downflow is most common. Flow rates are more critical on upflow operation, since they must be low enough to prevent channeling. Flow of solution through the bed may be by force of gravity or under pressure. Open tanks may be used for gravity operation, but where contamination of the solution might occur, these are not desirable. Pressure operation, more generally used than gravity, requires the use of closed vessels.

The depth of the exchanger bed is usually determined by the quantity and nature of the ions to be removed and the length of operating cycle desired. In



*FIGURE 3 - TYPICAL FIXED BED  
ION EXCHANGE UNIT*

commercial installations the bed depth is seldom under 30 inches, and for non-water softening applications, especially, bed depth is usually greater than this. Above the bed, a freeboard or rising space of 50 to 100 percent of the bed depth is provided to permit bed expansion without resin carry-over during the back-washing step.

External piping to the column usually connects to multiport valves which control each step in the operating cycle. These can be operated manually where the cycle is long, but the trend is toward greater use of automatic control. These valves not only introduce and withdraw the proper solutions during a given step, but also operate the steps in the proper sequence and for the proper period of time. The cycle can be controlled by a timing device, by volume measurement, or by pH or conductivity devices.

In addition to the above, fixed bed exchange units usually require such accessories as regenerant tanks, waste discharge sumps and pumps.

Recently, certain variations for the standard fixed bed ion exchange units have been developed. These hybrid designs employ such schemes as mounting several columns on merry-go-round like frames for continuous operation or employing rotary filter type drums with segmented compartments to effect continuous operation. (55, 56, 57, 87) Although these various developments have certain minor advantages, the ion exchange design engineer has usually chosen normal fixed bed operations as described above.

Fixed bed design calculations depend primarily upon such variables as the breakthrough capacity desired and the economic factors of resin utilization and regenerant efficiency. By knowing these and auxiliary information concerning resin specifications and flow rates, it is possible to calculate the bed dimensions. See references 6, 17, and 58 through 65.

### III. Continuous Countercurrent Ion Exchange (50)

Continuous countercurrent ion exchange is not a new idea. As early as 1921, C. H. Nordell applied for patents for continuous water softening apparatuses, using natural zeolites, although these systems apparently were not accepted for general use. (88, 89) With the advent of the high capacity, bead-

form resinous exchangers, however, continuous systems became more feasible because the resins can be handled by fluidizing in water without great attrition losses. (66)

Continuous countercurrent ion exchange implies the continuous counter-current flow of the exchanger and solution through some contacting device as indicated schematically in Figure 4. This process offers a means of utilizing regenerant chemicals more effectively. Also, it generally uses less exchanger and rinse water and its equipment may be more compact than that of either batch or fixed bed methods. Since saturation and regeneration are necessarily carried out in separate sections, each section can be designed specifically for the most efficient operation, whereas in fixed bed ion exchange, the geometry of the resin bed must be a compromise between the ideal for saturation and that for regeneration.

#### A. Equipment

##### 1. Hydro-Softener

In spite of the obvious advantages of a continuous contactor, only one commercially successful ion exchange unit which is truly continuous and counter-current in operation has been designed to date. This is the Dorrco Hydro-Softener (90). This unit is used primarily for softening water by fluidized contact between the water and a bed of resin in the larger of the two tanks which comprise the unit. As the resin becomes exhausted, it is transferred from the softening tank to the regeneration tower by means of ejectors. Since the concentrated regenerant brine has a lower volumetric flow rate, the regeneration unit can have a smaller diameter, illustrating the advantage of having separate functional sections. As the resin settles in the regenerant tower, it is washed free of salt near the bottom before it is recycled to the softening tank.

A pilot plant unit of the Hydro-Softener used to soften water at Baxter Springs, Kansas, consists of a softening tank six feet in diameter and a regenerant tower only 22 inches in diameter. Operating with 84 cubic feet of Nalcite HCR resin and a flow rate of 170 gpm., this unit is capable of reducing the hardness of water from 160 to 4 ppm.  $\text{CaCO}_3$  at a salt efficiency of 50 percent, and a resin utilization of only 10 percent of capacity. (50)

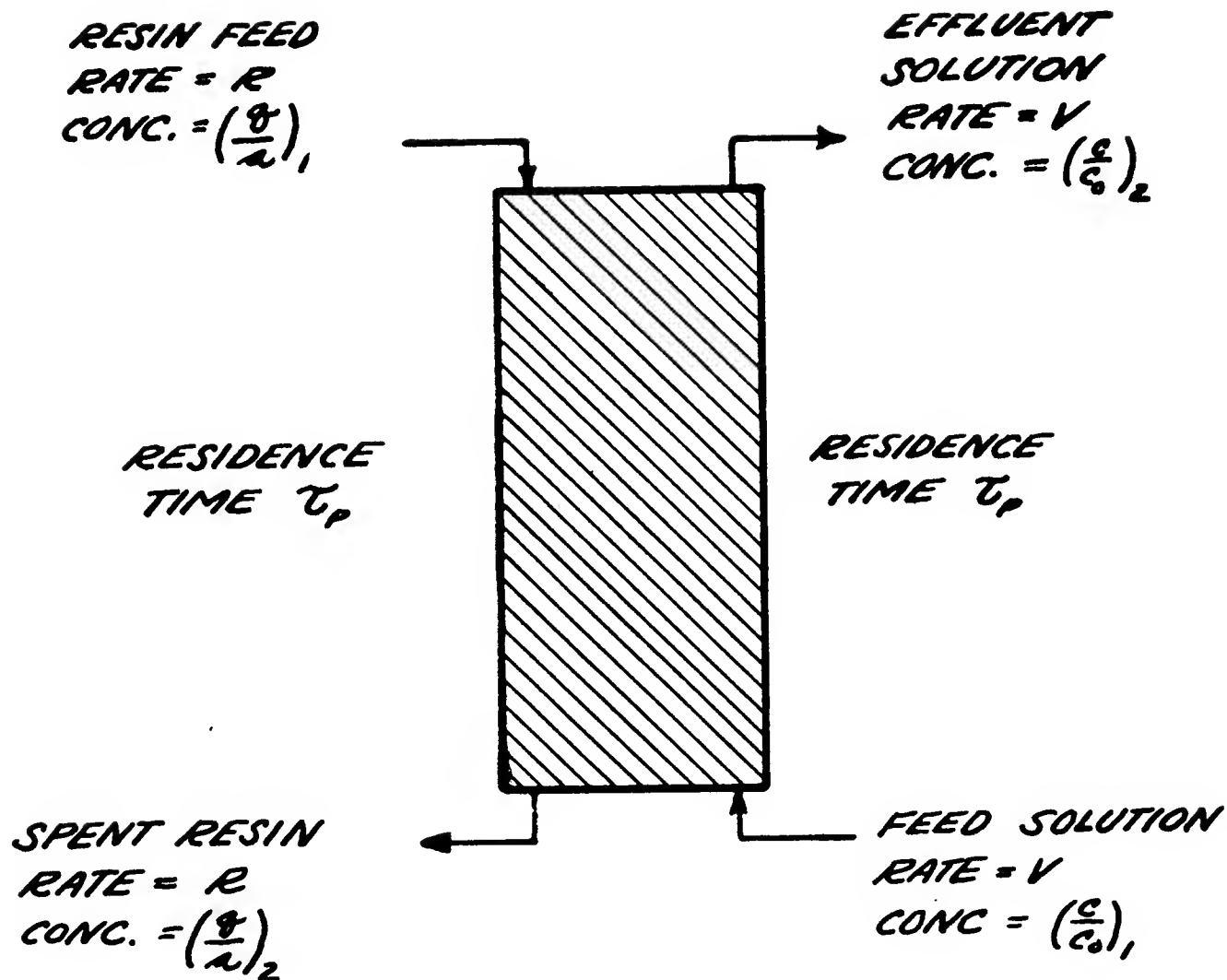


FIGURE 4-SCHEMATIC DIAGRAM FOR  
SIMPLE COUNTERCURRENT ION EXCHANGE  
OPERATIONS

This method of continuous ion exchange has not been commercialized more extensively primarily because of the inherent mechanical and hydraulic difficulties in obtaining satisfactory contact between a counter-flowing liquid and a subdivided solid. Those problems to be overcome include those associated with the small density difference between a resin and solution, attrition of moving resin (although reportedly only 10 percent per year), separation of the two phases after contact, and channelling and distribution of the two phases through the contactor. Also, solution flow rate may be limited by carry-over of resin from the top of the contactor (termed flooding). The recommended maximum flow rate for this type of unit is 7 gpm. per square foot of area when treating water in an upflow fluidized bed of nuclear sulfonic type resin, having a true density of about 80 pounds per cubic foot when wet.

Usually contact in a fluidized bed, as above, is effective only where there is an extremely favorable equilibrium such as exists for the  $\text{Ca}^{++}$ - $\text{Na}^{+}$  exchange in water softening. In other processes such as metal recovery from ore pulps, or treatment of plating waste solutions, plug or piston flow of the resin must be used in order to attain a sufficient degree of exchange. In such cases, the flow rate must then be held below 3.5 to 4.0 g.p.m. per square foot, in order to avoid fluidization. In the case of anion exchange, the flow rate must be even less, since the density of these resins is only about 70 pounds per cubic foot.

Some solutions to this flow rate-density problem might be to:

1. Operate with solution down flow or horizontal flow.
2. Convey the resin through the contactor by mechanical means.
3. Prepare denser resins.

## 2. Pulsed-Bed Continuous Column

A type of contactor which tends to solve the flow rate problem is that developed by I. R. Higgins and co-workers at the Oak Ridge National Laboratories. Although still in the development stage, it is felt that if this method of operation can be applied in large diameter columns, a successful commercial unit can be developed. In the Higgins contactor, movement of the resin upward through the column is accomplished by application of hydraulic impulses to the base of the resin bed, as shown in Figure 5. In operation, the resin and solution



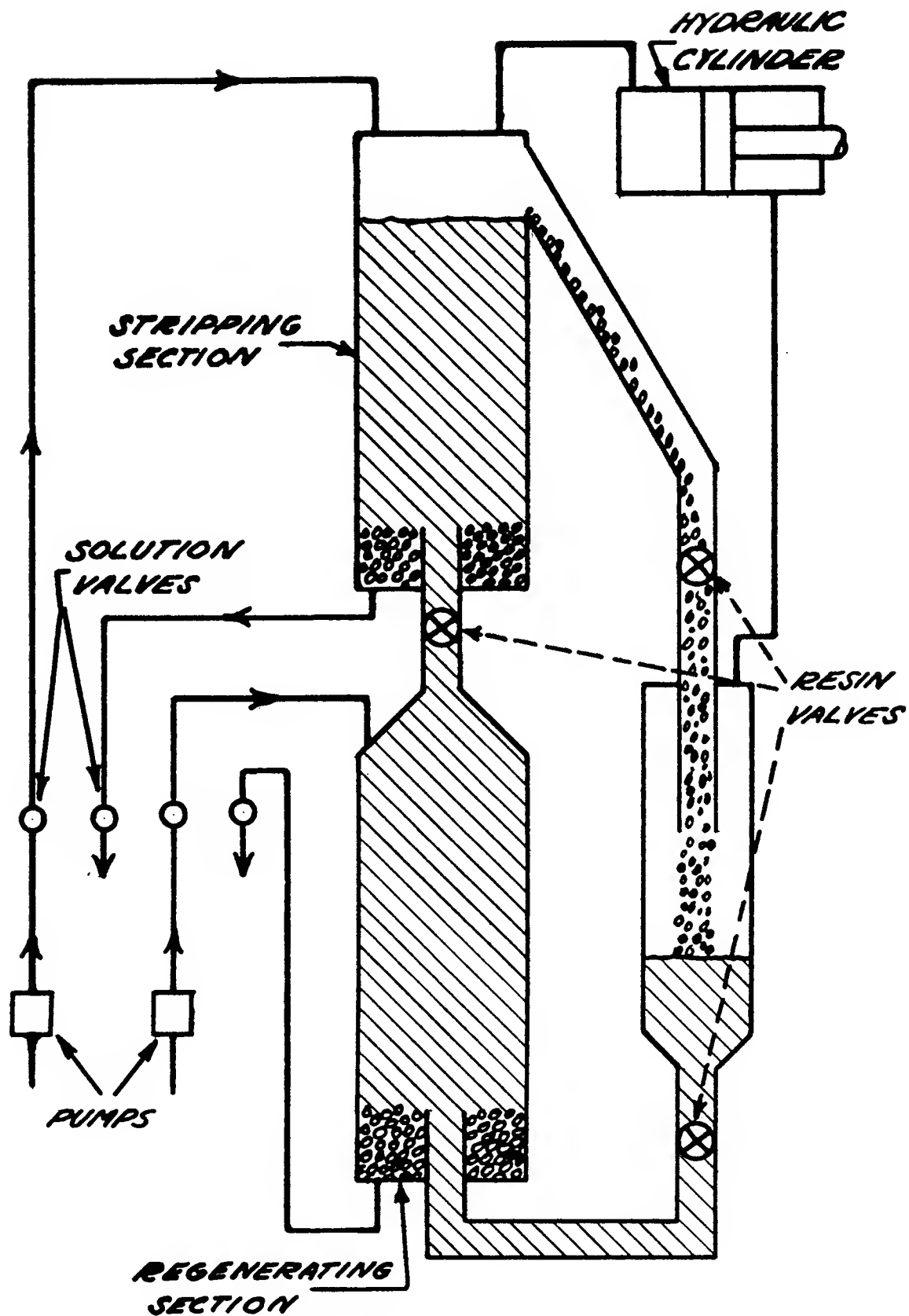


FIGURE 5-DIAGRAM OF A PULSED-BED CONTINUOUS ION EXCHANGE SYSTEM

alternately flow countercurrently through the column. During the short period of several seconds in which the resin is forced an incremental distance up the column, the solution flow must be interrupted. Then the solution is passed downward through the stationary resin bed for a predetermined interval of several minutes. Cycles are so short that the device is essentially continuous. Satisfactory separations of similar cations such as sodium and lithium have been carried out in this apparatus.

### 3. Ore-Dressing Jigs (68, 69, 70)

Another type of equipment which has been proposed for continuous counter-current ion exchange is a type of modified ore dressing jig as shown in Figure 6. This device, contrived by McNeil, Swinton and Weiss, operates on the solution upflow principle. The pulsations of the diaphragm at the bottom of the jig induce alternate expansions and contractions of the resin bed on each screen. The resin gradually becomes exhausted as it cascades slowly down the column from one screen to the next. Exhausted resin is carried from the bottom of the unit by an ejector to a rotary vacuum filter. The de-watered resin falls into a regenerating unit, which is of the swinging sieve jig type, for regeneration to its initial form by countercurrent contact with regenerant solution (See figure 7). The main advantage of this swinging sieve jig is that the flow of resin is horizontal, so that very little elevation of the resin is needed between rinse and regeneration sections.

Resin leaving the jig is de-watered on a second rotary vacuum filter before return to the saturating jig. Another advantage of the method is that the resin is in a semi-fluidized state on the sieve, and hence anion resins could be regenerated with inexpensive lime slurries. Similarly, various leach ore pulps can be treated directly, without filtration.

Equipment of the ore dressing and swinging sieve jig type is commercially available in large capacity sizes from mine equipment manufacturers. Although the efficiency of the ion exchange is not too high in this process, it is felt that this is balanced by the ruggedness, flexibility and ease of maintenance of the equipment. (50, 68)

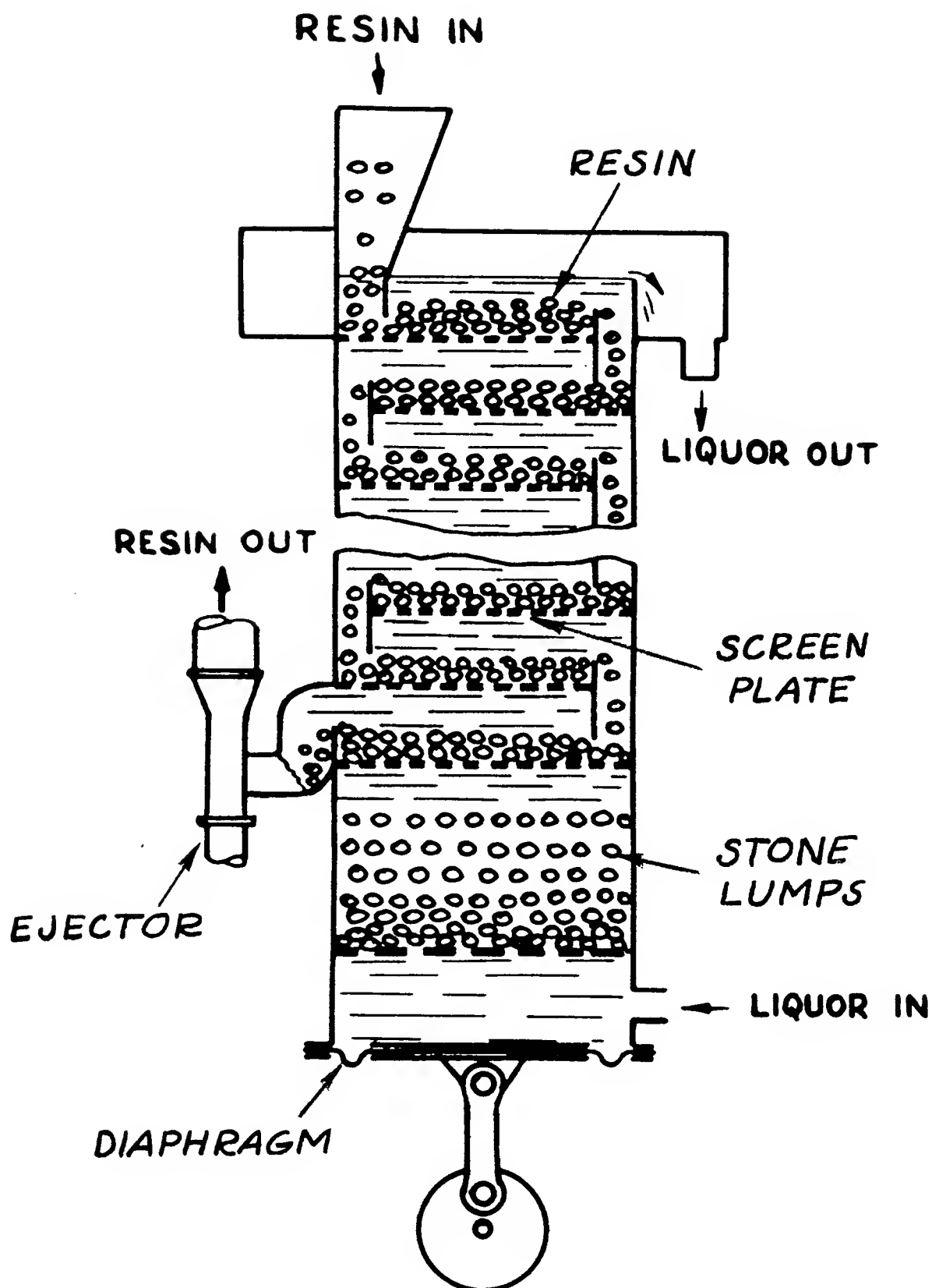


FIGURE 6 - DIAGRAM OF A TOWER TYPE  
MODIFIED ORE DRESSING JIG

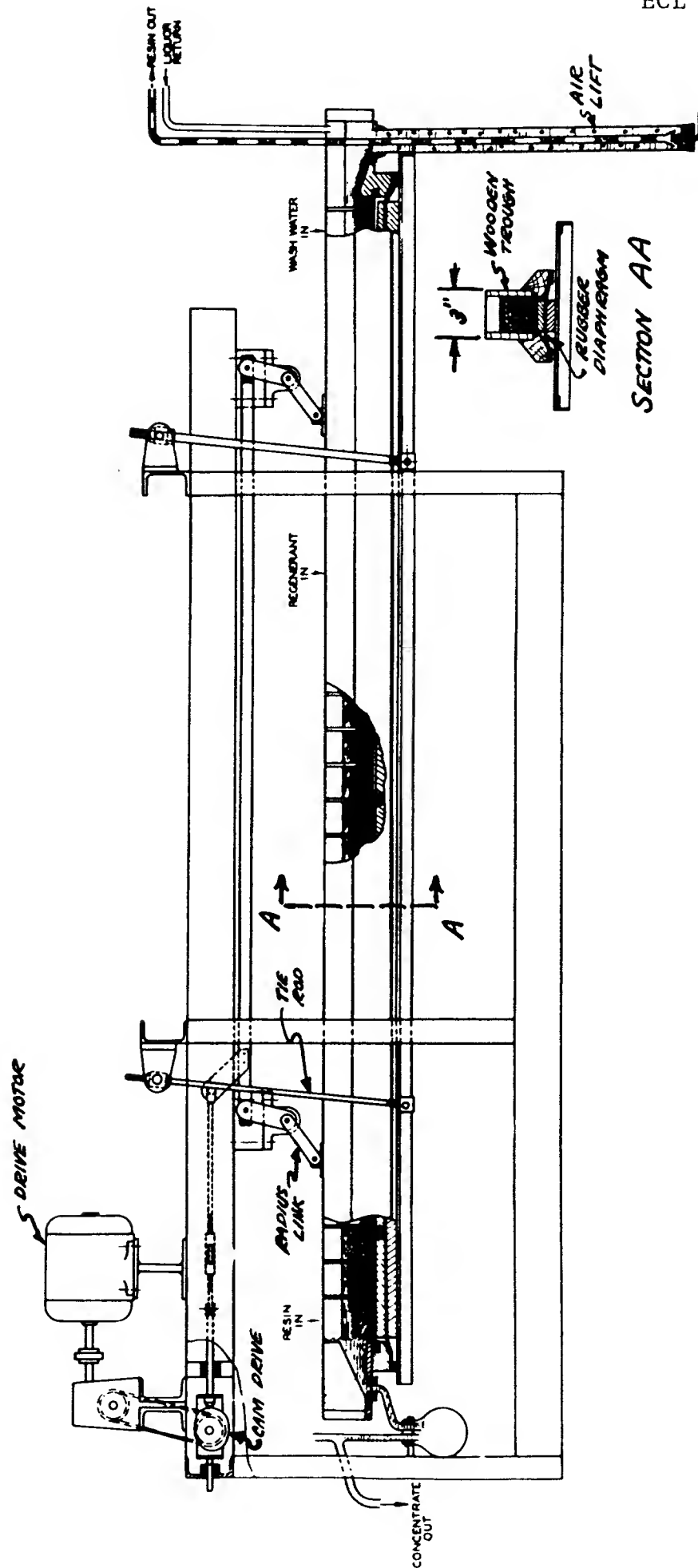


FIGURE 7-SWINGING SIEVE JIG

#### 4. S.I.R. Continuous Ion Exchange Column(71)

At Stanford Research Institute, continuous countercurrent ion exchange has been carried out successfully in a glass column, 4 inches in diameter, (see Figure 8). A unique feature of this unit is the two, rotating valves, provided for de-watering and metering the resin to and from the column. These motorized resin valves are similar to one developed by Stanton (72), as shown schematically in Figure 9. Also, a similar column and valve arrangement has been patented recently by McIlhenny and McConnell (73).

Most of the experimental work carried out with this apparatus involved transfer between alkali metal ions in the rising solution and hydrogen ions on the descending resin. Contact between the two phases occurs in the dense bed of resin, moving as a piston through the column. The upper valve continually supplies resin to the top of the moving bed, while the lower valve withdraws it at the same rate, maintaining a constant bed height. Resin entering a rotating valve is retained on the perforated glass disk at the midpoint of the bore. Free solution drains through this disk. As the bore passes under the right air inlet, air pressure applied by means of a cam-actuated solenoid valve de-waters the resin by forcing the remaining interstitial solution through the perforated disk. Upon further rotation of the valve, the bore becomes aligned with the outlet port and wash solution displaces the resin slug and carries it out as a slurry. Any remaining wash solution is forced from the bore by air pressure.

Another unique feature of the S.I.R. unit is the insertion into the column of a set of tiered screens with perforated openings, slightly larger than the largest resin particles, (See Figure 10). A central rod passing through these screens is tapped by means of a cam-actuated hammer, in order to vibrate the centers of the screens, and effect reorientation of the resin particles, and thus reduce channelling as the resin migrates down the column and through the screens. At solution flow rates below those which cause expansion of the resin bed, (0.6g.p.m per square foot.) this tapped screen device promotes contact efficiency between the solution and the resin. However, when solution velocities are high enough to maintain the resin in an expanded, but still not fluidized condition, (up to 3.5 g.p.m. per square foot), the contact is equally good with or without the screen assembly.

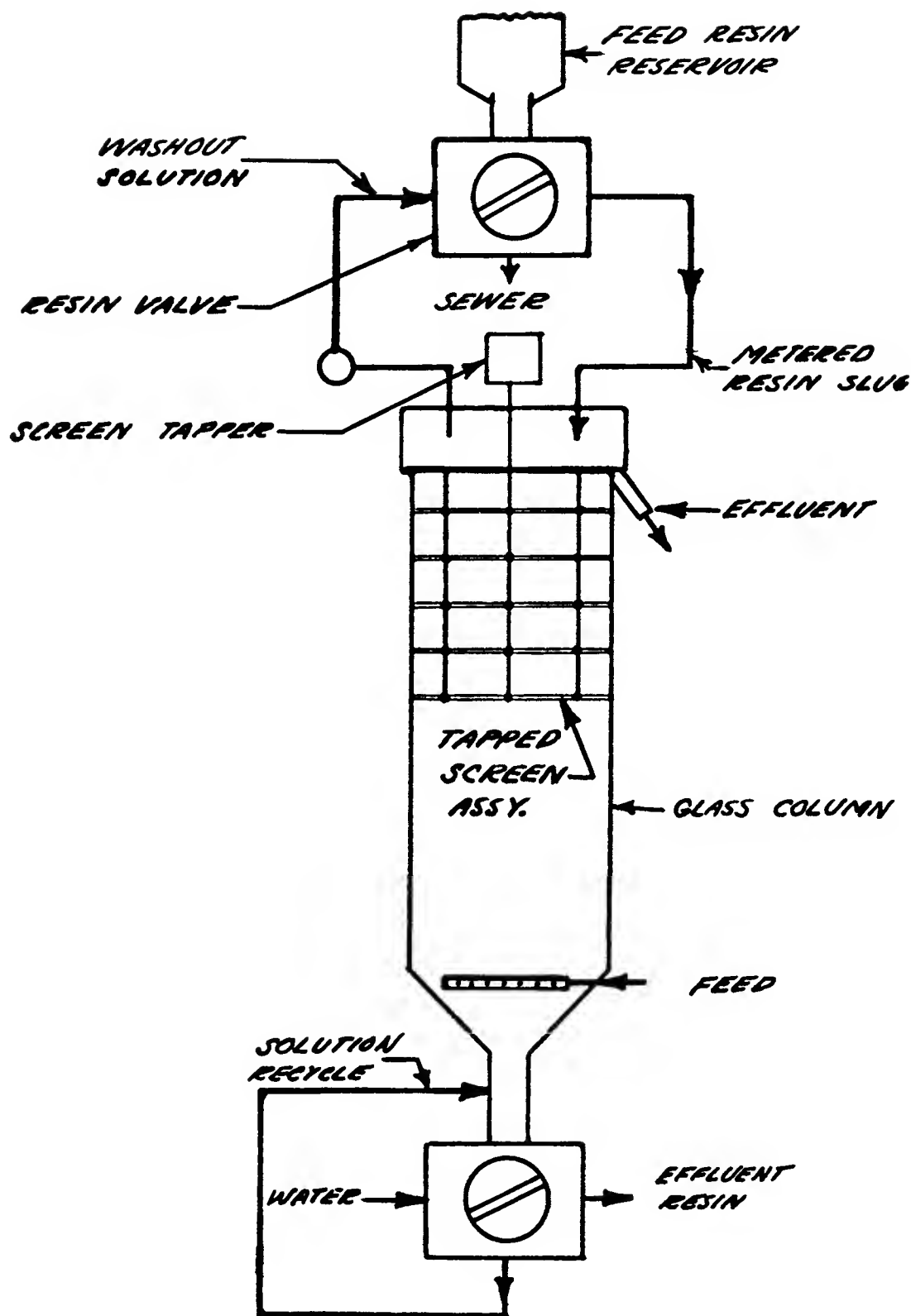


FIGURE 8 - SCHEMATIC DIAGRAM OF S.R.I.  
CONTINUOUS ION EXCHANGE COLUMN

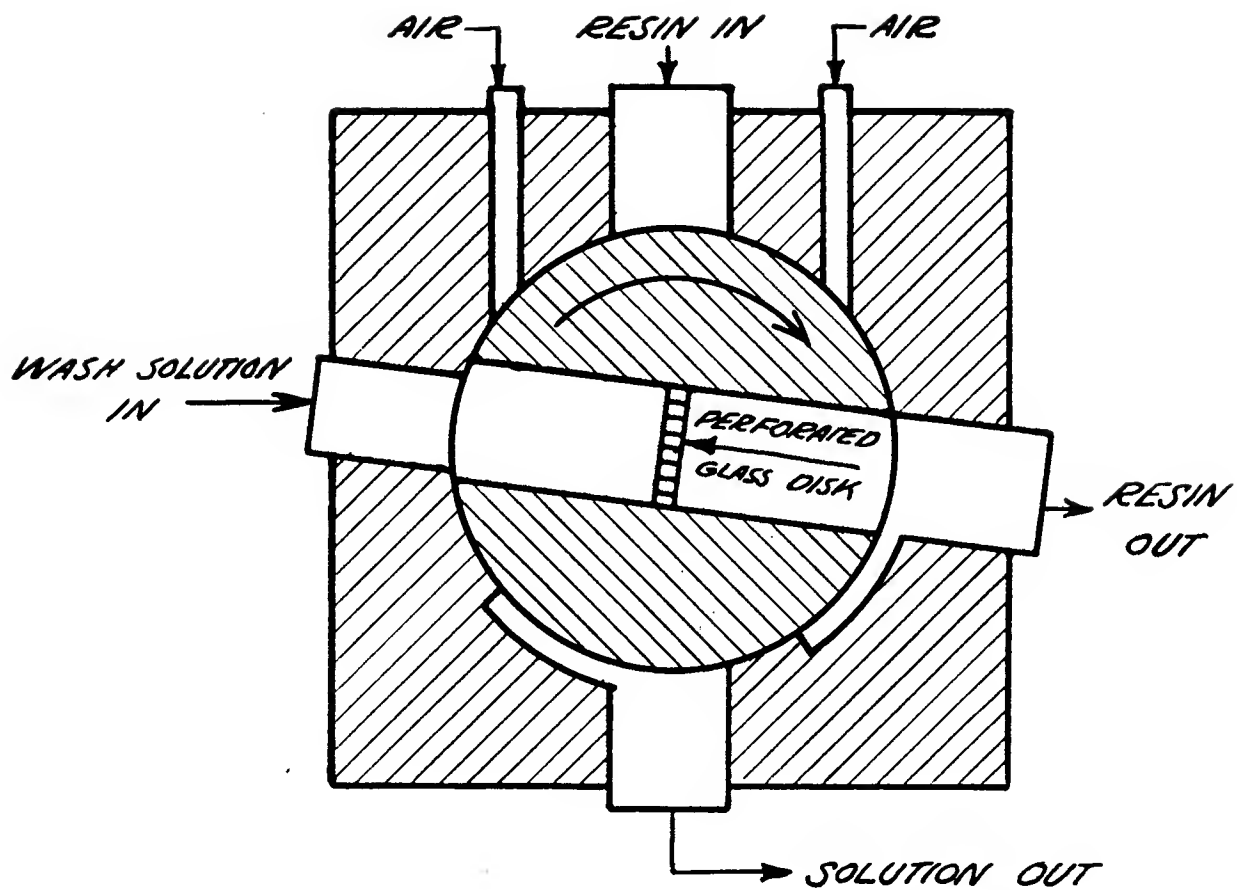
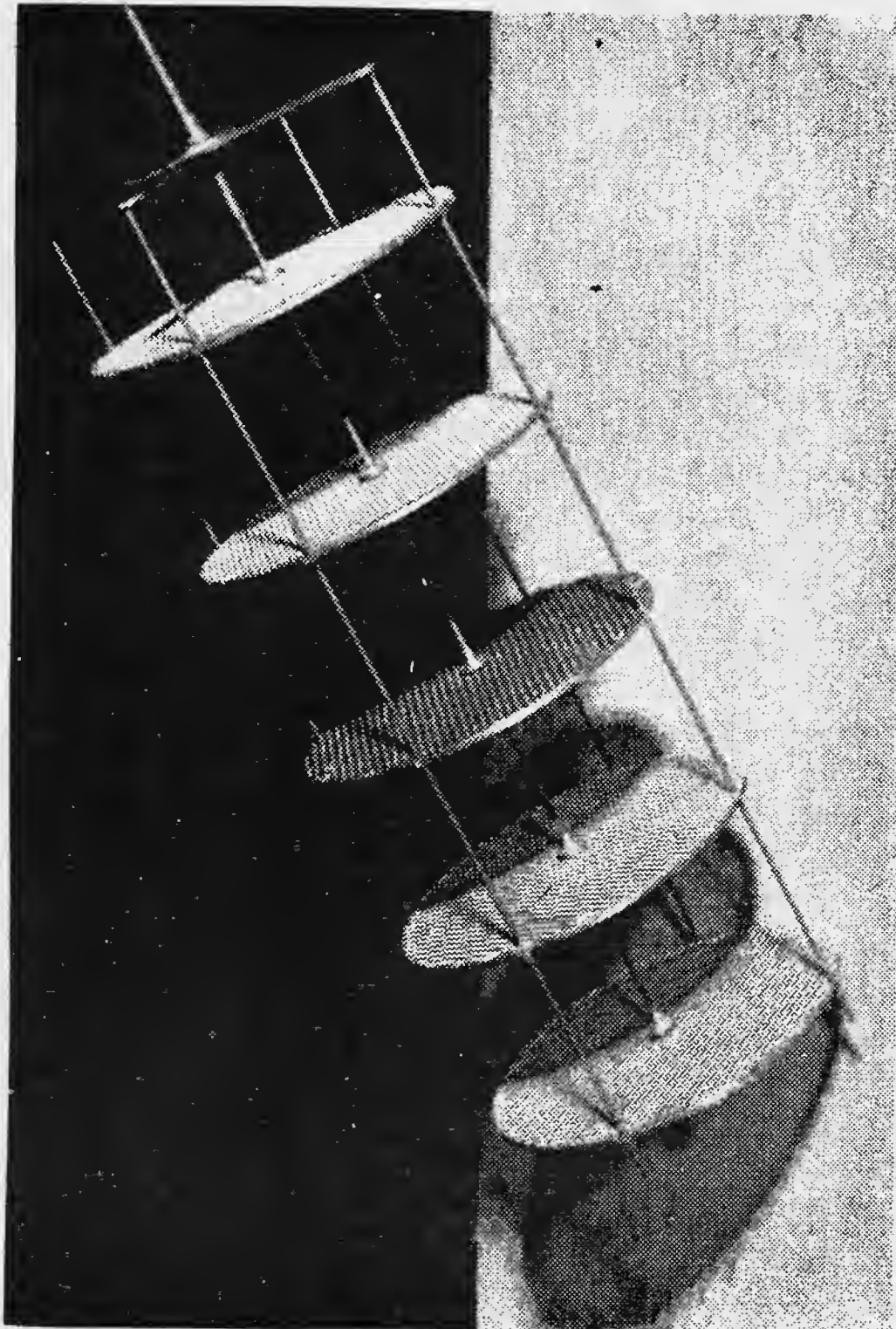


FIGURE 9 - SCHEMATIC DIAGRAM OF  
RESIN METERING AND DEWATERING VALVE



*FIGURE 10 - S.I.R. TAPPED SCREEN ASSEMBLY*



Results from experiments using the above equipment showed that this type of continuous apparatus was less efficient than a fixed bed column, operating under the same conditions. In spite of this inherent inefficiency, however, it has been demonstrated that resin and equipment requirements for a continuous countercurrent column of this type are much less than for an equivalent fixed bed unit.

#### 5. Miscellaneous Experimental Devices

In addition to the above described equipment, there also exist other devices for effecting continuous countercurrent ion exchange which have been devised by various persons interested in the development of the process. One such device was developed by McCormack and Howard at the University of Detroit (74). Their unit consists of cation resin enclosed in a porous flexible casing, and conveyed like a continuous string of sausages through a series of three tubular liquid reservoirs, (see Figure 11). The first reservoir is the feed exchanging section in which the ion to be recovered is removed from the feed solution by the slowly moving bundles of resin. The next reservoir is the regenerating section in which the exchanged ion is recovered from the ion exchange bed as product solution. The last reservoir is a rinsing section to remove adherent regenerating solution from the resin bed. These reservoirs are sized to fit as closely as possible around the moving bed, to prevent solution by-passing the resin, and are shaped to the sag of the resin bed between the drive wheels and the idler, so as to minimize the drag of the bed against the tube walls.

Continuous ion exchange may be carried out in a similar manner by the use of an endless belt of phosphorylated cotton using a process developed by Muendel, Selke and Guthrie, (26, 75). The equipment of this process consists of a 5 inch wide, endless belt of the ion exchange cotton which is passed countercurrent to streams of the feed solution flowing in 30 inch long shallow tanks containing baffels. On the other hand, two Japanese researchers (76) circulated an endless wire mesh, coated with ion exchange resin through adjacent saturant and regenerant tanks in a similar manner.

Another laboratory system for continuous ion exchange, developed by Selke and Bliss (66) for the recovery of copper from dilute solutions, consists of

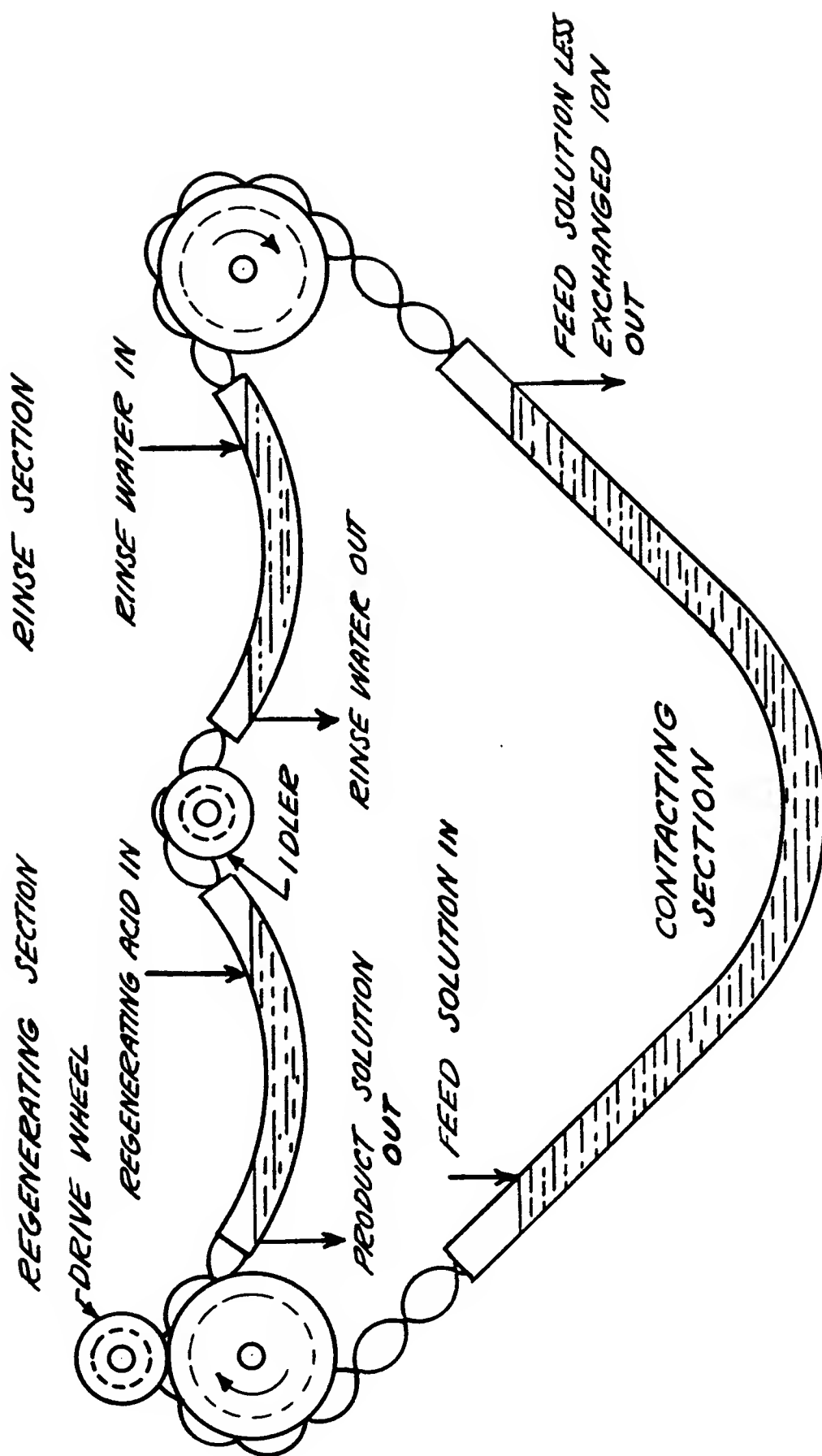
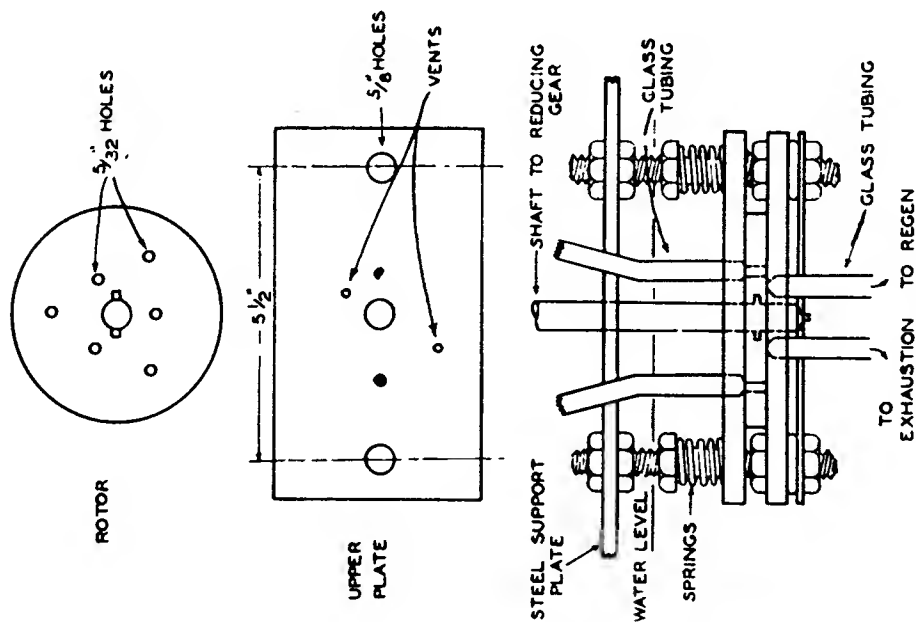
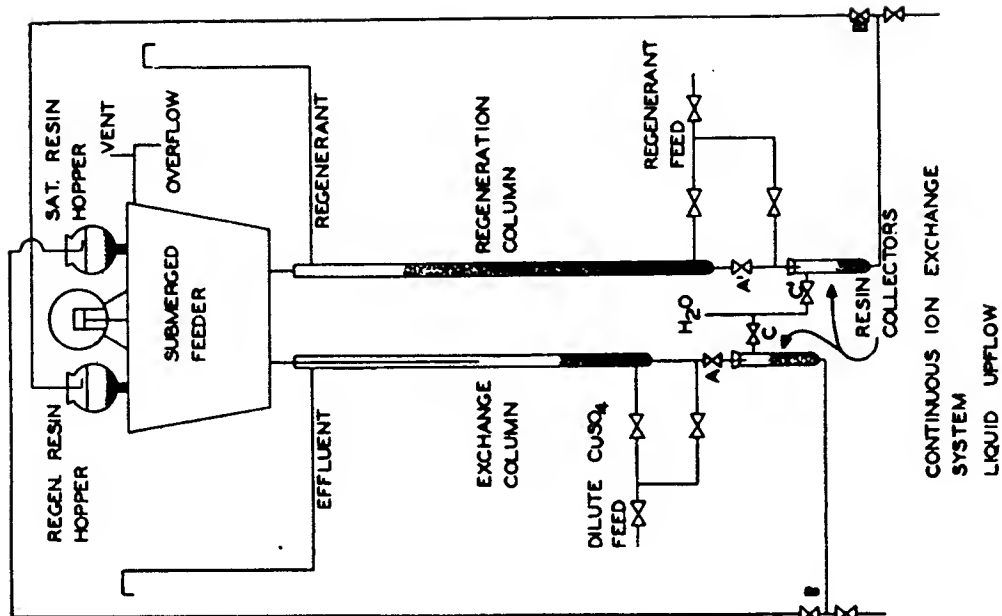


FIGURE 11-CONTINUOUS COUNTERCURRENT ION EXCHANGE UNIT



**FIGURE 12-SELKE AND BLISS ROTARY FEEDER AND CONTINUOUS ION EXCHANGE SET-UP**

transferring hydrogen-form resin into the exchange columns by a rotating disk feeder as shown in Figure 12. Velocity of the rising solution is maintained high enough to fluidize the entering resin. Countercurrent operation is obtained by virtue of the greatly increased density of the resin as it adsorbs more and more copper ions from the feed solution. This hydraulically classifies the resin in the fluidized bed for discharge of the heavier exhausted resin from the bottom of the column. By extrapolation of the experimental operation of this equipment, it appears that a continuous system of this type containing 1,500 pounds of resin would be equivalent to a fixed bed system with two 5,000 pound beds for the concentration of 1,000 gallons per day of 0.1 normal copper sulfate solution. (66)

In addition to the above devices, several methods for the mechanical conveyance of the resin, countercurrent to the solution, have been attempted. A screw type device, similar to that used in a coal stoker, seems to be practical, but in practice, it causes excessive attrition of the resin and short circuiting of the two phases past each other, unless close tolerances and sealing precautions are observed (77). Some potential continuous ion exchange devices might be patterned after the designs of any of the solid-liquid contacting devices used for the countercurrent extraction of oil seeds, adsorption of liquids or leaching of ores (78, 79, 80, 81, 82, 91, 92). In a recent patent (93), D. W. Collier has proposed six different combinations of various standard pieces of apparatus which could be employed in the treatment of liquids with ion exchange materials, and these six methods are essentially continuous. Unique feature of Collier's patent is that both anion and cation exchange resins may be used simultaneously.

Another type of continuous exchange apparatus used by W. W. Koenig in his investigation of ion adsorption, was a spinner column, consisting of an inner cylinder, rotating on a vertical axis inside a vertical column, with liquid and resin flowing countercurrently in the annular space. In his experiments, Koenig used two columns: one for contacting, and one for regeneration. The columns consisted of Pyrex pipes, three and one half and four feet long, and three and six inches in diameter. Rotors of varying size were constructed as smooth

cylinders of wood and steel and covered with corrosion resistant paint. Resin entered the columns at the top, through stainless steel funnels and settled downward, by gravity, through the annular space as shown in Figure 13. At the bottom, exhausted resin was removed by air lifts and transported to a 100 mesh, endless belt screen where it was drained nearly free of solution, and then blown, by air jets, into the funnels of the regeneration column (83).

Although there probably exist various other laboratory and experimental devices for conducting continuous countercurrent ion exchange, it is felt that any variations to be found are more or less minor, and all basic types have been mentioned above.

#### B. Design Problems (50)

It is not usually a difficult matter to design a piece of equipment to perform a single, basic operation. However, in the case of continuous countercurrent ion exchange, such a piece of equipment is not feasible, since a multiplicity of operating conditions must be met satisfactorily. This means that it may be necessary to compromise the conflicting choices which have to be made. For example, while it would be desirable to use high solution velocities in the contactor unit in order to minimize cross-sectional area and reduce fluid film resistance to ion transfer, the linear solution flow rate is limited by carry-over of the resin in the solution upflow type of device, and by excessive pressure drop in the downflow type. The limit in each case is about 7 g.p.m. per square foot. A very nice compromise of this situation, it would seem, would be to transport the resin, by mechanical means, in porous fabric casings or screen baskets, through a horizontal contactor in which the flow rate is limited only by the degree of exchange or ion removal desired.

In continuous ion exchange as in any other method of ion exchange, there is no way of controlling the resistance of the resin to internal diffusion of ions except by changing the particle size. The objective, therefore, is to minimize the external film resistance, and make the internal diffusion rate the limiting factor for exchange velocity, and thus achieve the lowest height or shortest length of contactor as possible. In order to achieve minimum film resistance, the solution flow rate should be as high as permitted by hydraulic limitations.

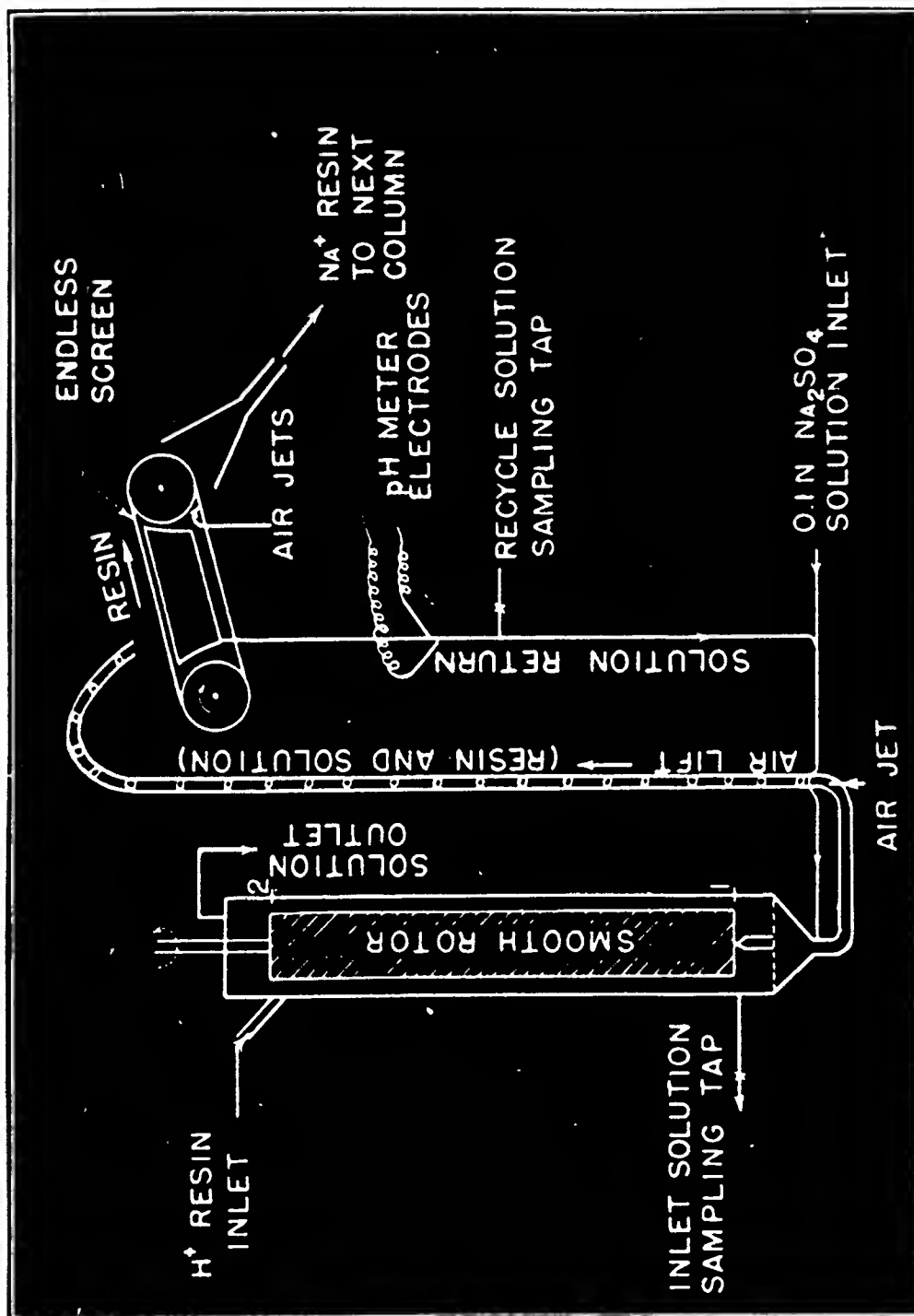


FIGURE 13 - KOENIG SPINNER TYPE COLUMN  
FOR CONTINUOUS ION EXCHANGE

The flow rate and the anticipated volumetric feed rate determine the cross-sectional area of the contacting unit.

Other design factors which will vary in importance, depending upon the type of contacting equipment used and the solution to be treated, include the following, which should all be minimized:

### 1. Attrition of Resin

In fixed bed practice, resin loss due to physical attrition is almost negligible, maybe one or two percent per year. Where recirculation of resin through a contactor is involved, however, attrition can be much higher and must be considered in design. Although most of the synthetic resins have some elasticity, they are subject to mechanical abrasion and destruction. Being homogenous, the resin particles are not affected by fracture as far as ion uptake is concerned, but the fragments may plug the system, or be carried out in the effluent and lost forever. At current prices of \$20.00 to \$50.00 per cubic foot, it does not require an extremely high attrition rate to turn a commercial ion exchange venture into an investors nightmare.

Usually, passage of a dense or a fluidized bed of resin through a single contactor does not, in itself, result in appreciable physical degradation. Primarily, it is the transfer of resin between contacting and regenerating units that leads to attrition. Whether resin is transferred as a slurry (by ejector, air lift, or direct pumping), or as a drained mass (by screw or travelling screen), attempts must be made to minimize transfer velocities, sudden changes in direction or mechanical crushing and abraiding. In the S. R. I. column, discussed on page 21, some measurable resin attrition occurred even in the tapped screen assembly, although the major portion of attrition, about 0.1 percent per pass, occurred in the resin transfer valves (See Figure 9). Attrition, in this case, would probably be even higher if a metallic ore pulp were being treated, because the suspended mineral particles in the pulp tend to "hydraulically sand blast" the resin particles in the countercurrent flow.

### 2. Channelling

Channelling, or non-uniform flow distribution of either solution or resin is another design factor which must be minimized in continuous countercurrent operation. Usually, the pulsating flow type of motion in modified ore jigs, or the

oscillating motion produced by a tapped screen assembly tend to reduce channelling and give uniform flow. In general, it has been found that the channelling problem is most acute where there is a change in the cross-sectional area of the contactor.

### 3. Contamination and Dilution

Contamination and dilution between the functional sections of a continuous ion exchange unit can result from ineffective de-watering of the resin between sections. Attempts to overcome this have resulted in the use of such devices as rotary vacuum filters, de-watering valves, endless screens and centrifuges in order to remove as much interstitial solution from the resin as possible before passing it on to the next phase.

### 4. Limitations on Particle Size Distribution

In order to avoid hydraulic classification, a very narrow range of particle sizes is required for successful fluidized contact. For solution flow through a moving, dense bed, however, the distribution of particle size is not so critical. In general, the narrower the range of particle size, the higher the cost of the resin.

### B. The Application of Continuous Countercurrent Ion Exchange to the Recovery of Metals from Ore Pulp

In general, the ore pulps to be treated contain approximately 25 percent suspended solids, much of which are in the form of slimes. The continuous countercurrent ion exchange process is particularly well suited for handling these pulps, since it eliminates the expensive preliminary filtering operation necessary in fixed bed concentration.

In a proposed method for utilizing continuous countercurrent ion exchange to recover metal values from an ore pulp, the metallic values are first brought into solution by leaching the ore with a solvent for the particular metal desired. For example, dilute sulfuric acid might be used to leach copper, or cyanide to leach gold. Then, the pulp and ion exchange resin are brought into intimate contact by passing them continuously and countercurrently past one another.



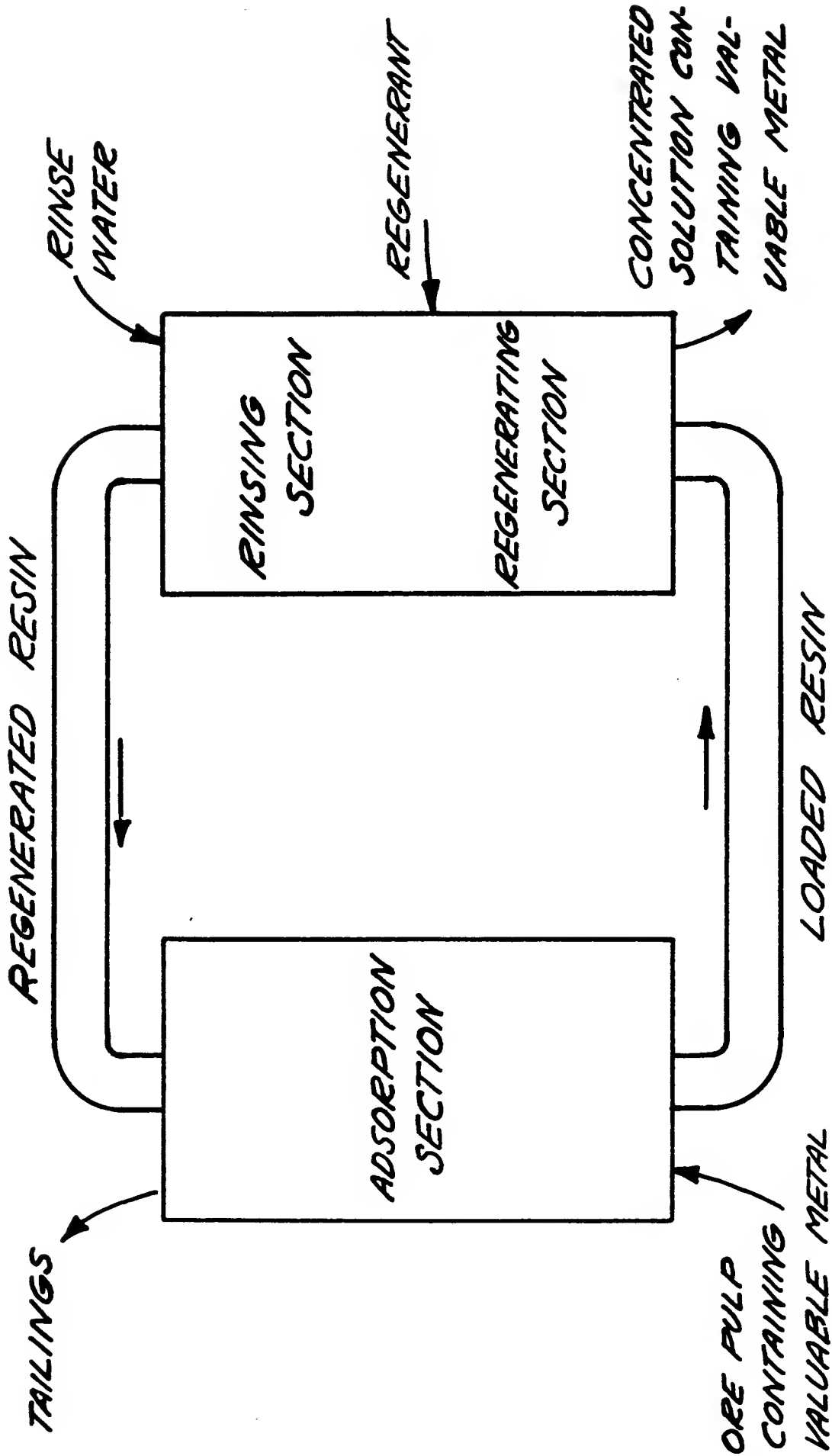


FIGURE 14- METAL RECOVERY BY CONTINUOUS ION EXCHANGE

The particle size of the resin in this case is about 20 mesh (833 microns), and the particle size of the solids in the pulp is about 100 mesh (148 microns) or smaller. After the resin has passed through the pulp and adsorbed the dissolved metallic ions, it is rinsed free of interstitial pulp and regenerated, also in a continuous countercurrent fashion. Such a process is shown schematically in Figure 14.

Since no quantitative data are as yet available for metal recovery from an ore by ion exchange, the design of continuous countercurrent equipment for such a process must be necessarily qualitative, placing little emphasis on relative size, capacity, flow rates and the like. The primary objective is to develop a practical type of mechanical device for continuously moving an ion exchange resin concurrently to a pulp. Consideration should also be given to the effective transfer of the resin from the contacting device to a continuous washing and regenerating device. In all instances, emphasis should be placed upon minimizing resin attrition and channelling of pulp through the resin.

One more fact which has bearing on the design is that the specific gravity of a 25 percent ore pulp is approximately 1.2, whereas the specific gravity of a resin particle is about 1.1. Under static conditions, therefore, the resin will float in the pulp.

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CONTINUOUS COUNTERCURRENT ION EXCHANGE

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